VOL. LIII, NO. 12, DECEMBER, 1958

THE Journal OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

PUBLISHED MONTHLY BY
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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII DECEMBER 1958 No. 12

CONTENTS

Some Notes on Thermal Unhairing - *By* RAYMOND HAUCK 676

Effect of the Moisture Content of the Leather on the Ball Burst Properties - - - - *By* MIETH MAESER 683

Life Lines - - - - - - - - - - - 701

ALCA News - - - - - - - - - - - 702

Patents - - - - - - - - - - - - 708

INDEX to Volume LIII - - - - - - - - 711

SUBSCRIPTION - - MEMBERS $12.00 A YEAR - - NONMEMBERS $15.00

Published Monthly by

The American Leather Chemists Association

Entered as Second-Class Matter at the Post Office, Easton, Pa.
Acceptance for mailing at special rate of postage as provided for in section 1103,
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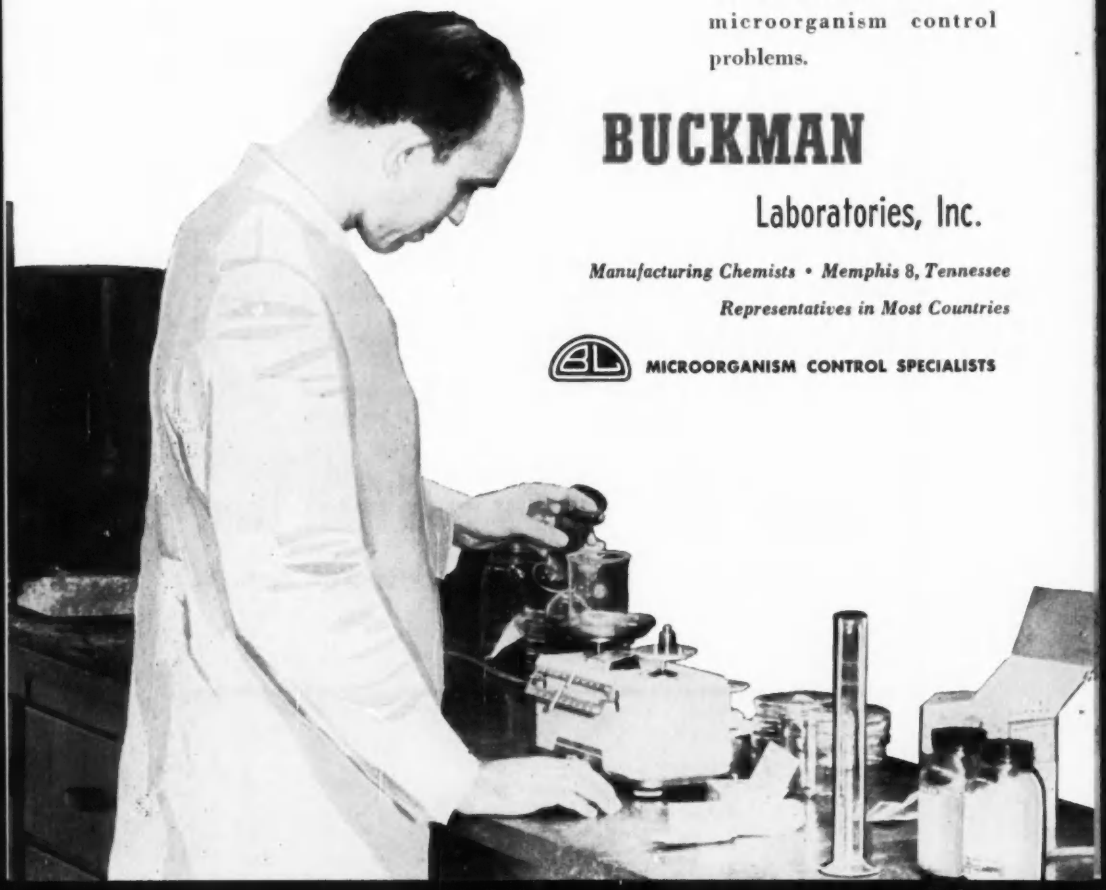

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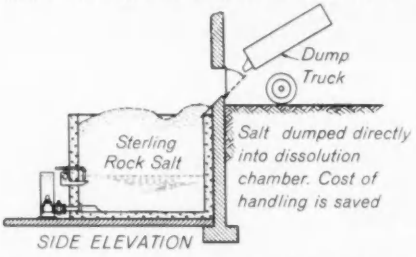
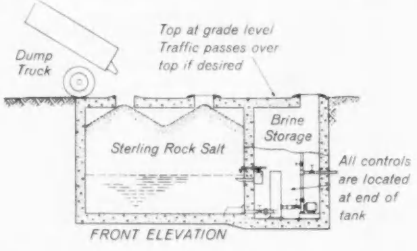


side property is not available. Salt is dumped from a truck directly into the dissolving chamber (the Lixator is just inside the plant wall), and salt-handling costs are reduced. The Lixator controls are easily accessible from inside the plant.

2. The Integral Brine Tank Storage Lixator . . . one of the best brine-making units for tanneries needing large amounts of fully saturated brine only at certain times. (The brine-storage tank included in the Lixator can be made as large as necessary.) Because the top of this Lixator is at ground level, traffic can pass over it — and delivery trucks can pour salt directly into the loading manholes.



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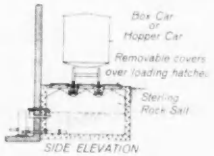

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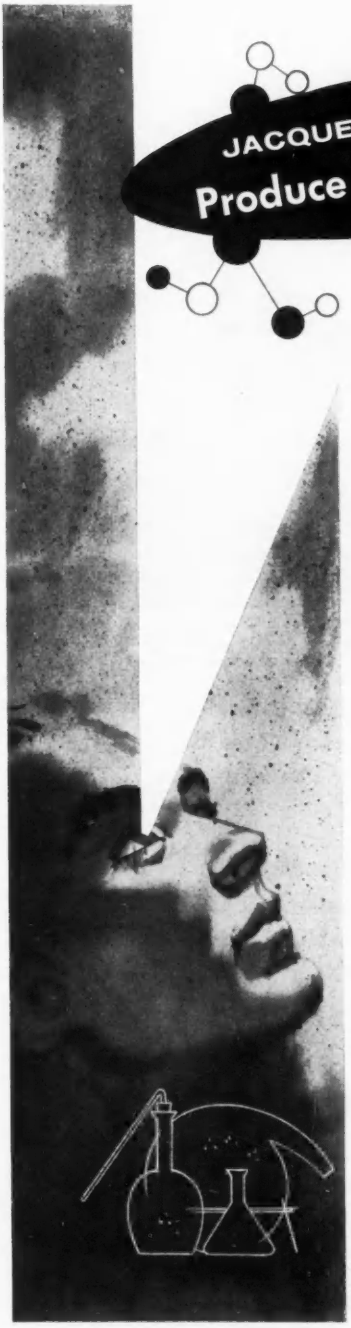

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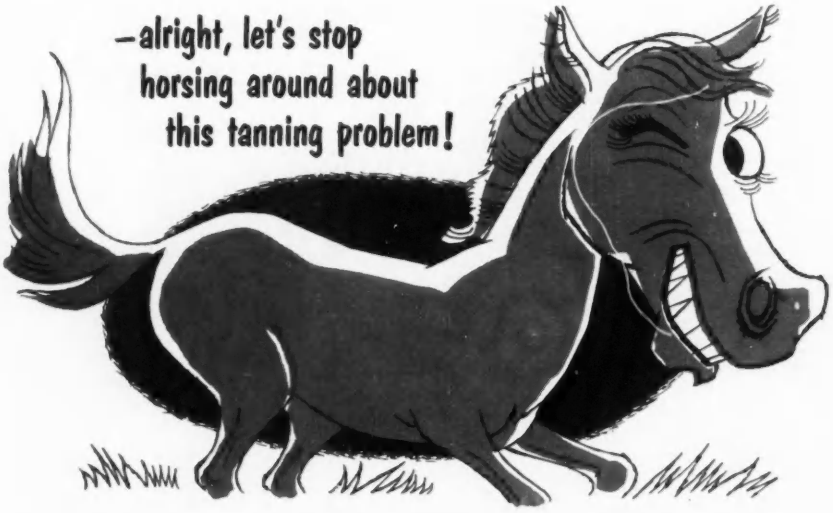

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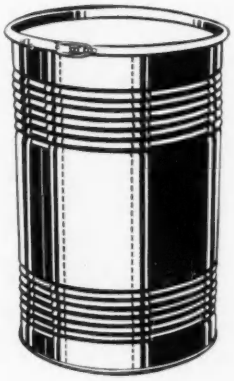

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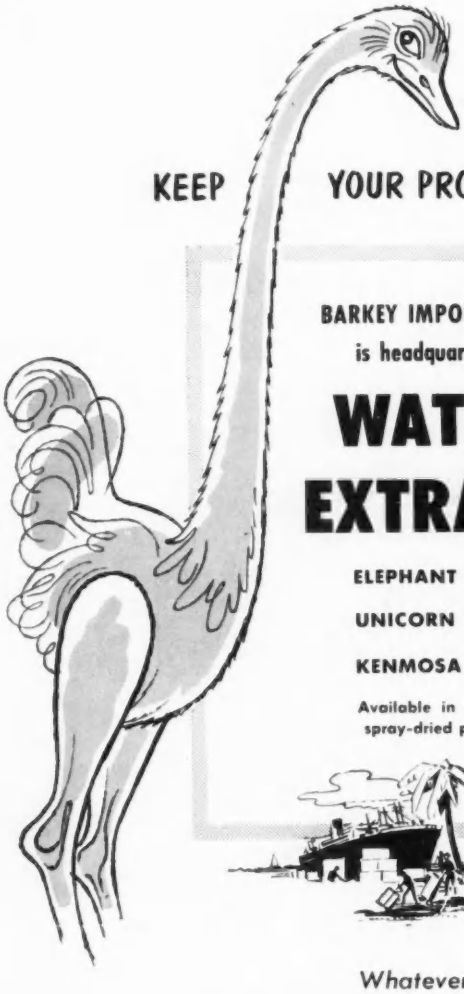

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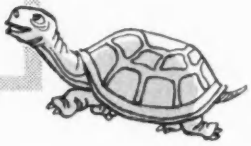

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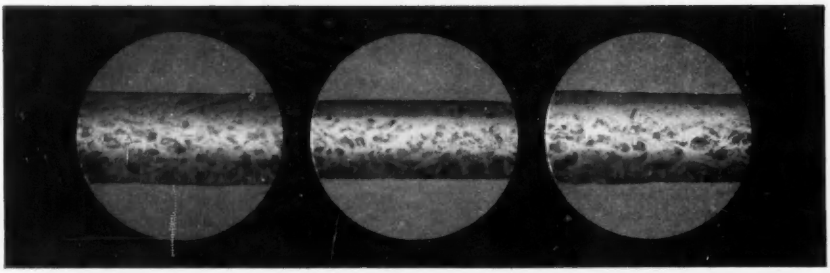

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General correspondence concerning the *Journal* should be mailed to the Managing Editor. Subscriptions—$12 per year for members; $15 for nonmembers.

SOME NOTES ON THERMAL UNHAIRING*

RAYMOND HAUCK†

Tanners' Council Research Laboratory
University of Cincinnati
Cincinnati 21, Ohio

ABSTRACT

The ability of an aqueous-thermal system to loosen hair of salt-cured stock sufficiently for mechanical unhairing has been investigated. Freshly flayed skin or hide can be unhaired after an immersion in 55°C. water for 15 minutes or in 60°C. water for 5 minutes, but salt-cured stock requires a 48-hour soak in mild alkaline solutions before equal unhairing can be obtained. The ease of unhairing skin or hide treated in the hot-water immersion system is less than that obtained by the conventional lime system.

—x—x—

INTRODUCTION

One general method of loosening hair sufficiently for mechanical removal during the beamhouse relies on agents which can destroy or modify the epidermal tissue surrounding the hair root (6). An aqueous-thermal system is one of the several different ways in which this loosening can be obtained.

The age-old process of scalding pigskin to remove bristles represents the common use of a hot-water system for unhairing. While the practice is capable of removing hair, frequently the action of the hot water damages the skin. Hausam (4) developed the "Dresden Process" for fresh pigskins as a procedure to reduce the incidence of skin damage due to hot water. Additional data are offered by Hausam (5) to substantiate his claim that under carefully controlled conditions scalding does not reduce the strength of the final leather product made from pigskins unhaired by the "Dresden Process". Results secured by Stather (9) on leather properties of scalded pigskins dispute Hausam's findings. Stather concludes that scalding is detrimental to the skins, and he condemns the practice. In a later paper Stather (10) presents further data concerning the effect of scalding on pigskin which also disagree with the results obtained by Hausam. Wang, De Beukelaer, and Maynard (11) studied the effects of time and temperature of the scalding bath on the tissue components present in hogskins by means of histological techniques. Their results, while not completely agreeing with Stather that scalding should be condemned and abandoned altogether,

*Presented as part of a thesis to the Graduate School of Arts and Sciences of the University of Cincinnati as partial fulfillment of the requirements for a Master of Science degree, June, 1957.

†This work was done under a fellowship granted by the Tanners' Council Hide Bureau, whose support is acknowledged in this publication.

nevertheless substantiate on a structural basis most of the claims made about hogskin damage resulting from the process.

Whereas considerable research has been conducted on the scalding of fresh pigskin, the hot-water system for unhairing fresh calfskin or cattlehide has not gone beyond the laboratory stage. Roddy and Jacobs (7) reported the unhairing of fresh cattlehide by treatment with distilled water at 60°C. Buechler and Lollar (1) also were successful in separating the epidermis from the skin by this method for their study of the sulfur distribution in the epidermis and hair of cattlehides.

These examples of unhairing fresh stock by means of hot water suggest that unhairing of cured stock should be possible by the same treatment. The cured stock requires an important additional step not necessary for fresh stock. This step is the rehydration of the cured skin or hide in a suitable soak liquor prior to treating the stock to the action of hot water. Without adequate rehydration the aqueous-thermal system used for loosening the hair will produce grain damage and collagen shrinkage of cured skin or hide.

EXPERIMENTAL

Our investigation of an aqueous-thermal system for unhairing cured stock included several aspects of study; the most important were the choice of an optimum time and temperature for the immersion bath and the choice of reagents for rehydrating the cured stock. Additional information was obtained on the effects of unhairing accelerators in this system and the relative ease of unhairing cured calfskin and cattlehide. The effects of these factors on the stock were observed grossly and histologically. The following paragraphs describe the experimental methods used and the results obtained.

Time-temperature studies of immersion were made with green salt-cured cattlehide. Specimens of cured hide were soaked for 24 hours in a 4-1 float of 0.1*N* sodium bicarbonate plus 0.05% Detergent A*; the liquors were decanted, and fresh liquors of a solution 0.1*N* with respect to both sodium bicarbonate and sodium carbonate were added for a second 24-hour period. After the second 24-hour soak, specimens were immersed separately for periods of 4, 5, 6, 7, 10, and 15 minutes in distilled water at 60°C. Other specimens from these same soaking treatments were immersed in distilled water at 58°C. for periods of 7, 10, 12, and 15 minutes. Specimens from a third group were immersed in distilled water at 55°C. for periods of 10, 12, 15, and 20 minutes. The specimens were then removed from the hot-water bath and laid out on a flat surface where they were unhaired with the edge of a blunt knife. When specimens were permitted to cool to room temperature before being unhaired with the knife, they were slightly more difficult to unhair than specimens that were unhaired before significant cooling had occurred.

*See footnote, page 678.

Unhairing trials of these specimens indicated that an immersion time of 6 minutes at 60°C. or 15 minutes at 55°C. permitted unhairing to occur. At these temperatures, less time did not allow sufficient loosening of the hair, and longer times resulted in a tightening of the hair and the possibility of grain damage. Thus these two conditions of immersion gave similar results and were considered to be optimum conditions to be used when evaluating other aspects of study. The unhairing results following immersion at 58°C. were less satisfactory than at either of the other two temperatures, as no suitable time could be found which would sufficiently loosen the hair.

After determining a suitable immersion time and temperature, various soak liquors were tested. These materials were screened for their ability to rehydrate cured skins or hide. These reagents were used in the soaks: water, sodium chloride, sodium polysulfide, sodium perborate, lithium chloride, dimethylamine, ammonium chloride, borax, sodium bicarbonate, ammonium bicarbonate, sodium carbonate, and ammonium carbonate. The soaking periods were for 48 hours with changes of soak liquor after the first 24 hours.

The screening of these soak liquors for their ability to rehydrate the skin or hide was confounded to some extent with various cures. Treatments were given to brine-cured calfskin, green salt-cured calfskin and green salt-cured cattlehide, all stored at 25°C. for 30 days; and to green salt-cured calfskin and cattlehide which had been stored at 0°C. for 30 days. A 24-hour soak of brine-cured calfskin in water, 0.1% polysulfide, 0.5% lithium chloride, or 1.0% ammonium chloride followed by a second 24-hour soak in 1.0% borax plus 2.0% sodium chloride resulted in subsequent unhairing after immersion in hot water. However, these soaking treatments did not rehydrate specimens from the other cure conditions sufficiently to permit unhairing. The only soaking conditions which gave favorable results for all types of cure consisted of sodium bicarbonate as the first 24-hour liquor and sodium bicarbonate plus sodium carbonate as the second 24-hour liquor.

To effect possible greater rehydration of cured stock, surfactants were added to the soak liquors. Nonionic wetting agents A, B, C, D, and E* were tested because of the alkaline nature of the soaks and the presence of amholytic proteins. An anionic detergent F* was combined with each of these nonionic surfactants to study its possible synergistic effect. These reagents were added only to the first 24-hour soak, only to the second 24-hour soak, in both soaks, in the hot-water immersion bath, and in all possible com-

*—The Commercial surfactants used were:

A a detergent and wetting agent of the fatty amide type—trade name: Alrosol.
B a nonionic-type detergent—trade name: Sandopan DTC-40.
C a 100% active nonionic polyoxyethylene thioether-type surface-active agent—trade name: Sterox S.E.
D an 85% active nonionic aliphatic polyoxyethylene ether-type surface-active agent—trade name: Sterox AJ.
E a nonionic-type detergent—trade name: Sandozin NI.
F an anionic alkyl aryl sulfonate-type surface-active agent—trade name: Santomerse.

binations of soaking and immersion. Comparisons on the effect of various concentrations were studied.

The concentration of the surfactant in the immersion bath was found to be critical. Small amounts, i.e., 0.05% to 0.1% on the solution basis, in the soaks improved rehydration to a degree, but any visible carry-over into the immersion bath resulted in tight hair. Thus, the most favorable results were obtained by using a surfactant in only the first 24-hour soaks. There was no measurable increase in the ease of unhairing due to any synergistic effect of a nonionic detergent and the anionic surfactant. Of the various surfactants screened, Detergent A gave the most satisfactory unhairing.

In conjunction with the mild alkaline soaks used to rehydrate the cured stock, various unhairing accelerators were added to promote rapid unhairing. Their effect on the subsequent ease of unhairing was noted. Mercaptoethanol, sodium polysulfide, sodium sulfhydrate, or sodium sulfide were added to sodium bicarbonate or ammonium bicarbonate to make the first 24-hour soak liquor. These reagents, in amounts ranging from 0.1% to 0.5% on the stock-weight basis, were used either separately or in conjunction with surfactants. Sodium polysulfide plus a surfactant with no additional alkali present in the soak was also used for a first 24-hour soak. Specimens of cured hide which had been soaked in these various liquors were then soaked for an additional 24 hours in one of the following: sodium bicarbonate–sodium carbonate, ammonium bicarbonate–ammonium carbonate, ammonium carbonate plus sodium sulfhydrate, or ammonium bicarbonate–ammonium carbonate plus sodium polysulfide. Although dimethylamine is not a reducing compound, it was included in this series because of its ability to accelerate unhairing in the conventional lime unhairing-system. Dimethylamine was added to the sodium bicarbonate–sodium carbonate second 24-hour soak for a stock that had been soaked the first 24 hours in sodium bicarbonate.

The addition of accelerators to the soaks did not improve the ease of unhairing cured stock when compared to skins or hides soaked in similar alkaline liquors minus the accelerators. Specimens which were soaked in solutions containing accelerators in only the first 24-hour liquors unhaired in all cases, but specimens which were soaked in liquors containing accelerators in the second 24-hour liquors unhaired unevenly. Although the results were quite variable with sodium sulfhydrate, it gave the best results of any reducing compound tested. The presence of an accelerator in the soaks increased the fine-hair problem. This problem was less pronounced in soaking experiments that did not contain accelerators.

Studies were conducted on the relative ease of unhairing cattlehide and calfskin in the thermal system. Both were soaked in similar liquors for 48 hours with a change of liquor after the first 24 hours. The first 24-hour liquor consisted of a 4-1 float of 0.1*N* sodium bicarbonate + 0.05% of Detergent A

on the solution basis. These specimens were then soaked a second 24-hour period in a 4-1 float of 0.1*N* sodium bicarbonate–0.1*N* sodium carbonate. After the second 24-hour soak each piece was immersed for 6 minutes in a fresh bath of preheated water kept constant at 60°C. The ease with which the hair was removed was judged and rated on the scale of poor, fair, moderate, good, and excellent, reserving the grade of excellent for cases in which the hair came out as well as from normal limed stock.

The repetitive trials indicated that calfskin is unhaired easier than cattlehide under the same conditions. The calfskin trials were all rated good, whereas only a few trials of cattlehide produced good unhairing, while other trials ranged from fair to moderate.

To study the effect of the hot-water immersion on cured stock, cross sections were prepared from a specimen of commercially green salt-cured calfskin which had been soaked for 48 hours in sodium bicarbonate and sodium bicarbonate–sodium carbonate, immersed in hot water at 60°C. for 6 minutes, and then unhaired. Cross sections were prepared from specimens kept in formaldehyde for 24 hours previous to sectioning. The cross sections were stained with haematoxylin and counterstained with eosin.

The presence of a large number of fibroblasts indicated that the calfskin was in a good state of preservation. The "*Erector pili*" muscles were in good condition. There was minimum alteration of the skin.

Evidently the hot-water treatment has no effect upon these cells. Except for the removal of the epidermis, hair, hair shaft, and roots, the cross sections have the appearance of green salt-cured calfskin that has received a normal 24-hour water soak. There is no indication of weakening at the juncture of the corium minor and the corium. The fiber bundles are less swollen, and the fibers in the bundles are not separated and opened up as well in the hot-water system as in the lime system. The stock is free of epidermal debris, but discounting the removal of the epidermis, the amount of globular protein removed from the grain area is negligible. However, the stock has a feel similar to bated stock; after unhairing, the stock retains the impression of the thumb. The alkaline soaks followed by immersion in hot water rupture the cells surrounding the hair root with perhaps no marked chemical action. The mild alkaline treatment rehydrates the intercellular cementing substance at the juncture of epidermis and corium, and the thermal methods permit mechanical rupture of the tissue surrounding the hair. Further evidence that the treatment is primarily effecting rehydration is derived from a study of the cross sections; these histological specimens show very little alteration of the skin components due to the hot-water unhairing treatment.

DISCUSSION

Histological studies of cross sections prepared from stock unhaired in the hot-water system indicate that the mechanism of unhairing depends upon

the rupture of the basal layer of the germinating cells of the epidermis and the softening and removal of intercellular substance at the epidermis–corium minor juncture. This mechanism would explain why there is nonuniformity of unhairing within various areas of the same piece and also between similarly treated pieces. The uneven effect of denaturation of the intercellular cementing substance during curing and storage would cause uneven rehydration. Cooper (2) has indicated that freeze-drying, the method which should cause the least denaturation of materials in bovine hide, effects the solubility of the noncollagenous proteins other than serum proteins of the ground substance and by this means reduces the rehydration of hide.

Selby (8) studied the skin of the rat and man by electron microscopic techniques and found the basal cell membrane to be bound to the dermal membrane by an amorphous material situated in a 300 A. space between cells and membrane. While this intercellular cement substance is soluble during the life of the animal, it becomes denatured and partially insoluble after flaying and subsequent curing in the case of bovine hide or skin. The hot-water unhairing treatment is capable of rehydrating and removing a portion of this material without causing much alteration to the other skin components, and thus permits unhairing by mechanical means.

Unhairing with lime alone or in combination with reducing compounds is explained by a different mechanism. According to a widely accepted theory the rupture of disulfide bonds results in accelerated unhairing. Vago (12) demonstrated that the reducing potential of sulfide is dependent on pH value, thus explaining why sulfides act on hair only at pH values above about 11. Gillespie (3) provided confirmation of Vago's findings during a study of the action of sodium sulfide on wool. This need for high pH values to give sufficient reducing potential to the reducing compounds tested may explain the lack of reactivity of these agents when added to the soak liquors for the hot-water system. The alkaline soaks used in the first 24-hour soak had pH values in the range 8.5–9.0; thus when small concentrations of reducing compounds were added to these soaks the resulting reducing potential was too low to accelerate unhairing. Experimental results indicate that immunization may take place if the reducing compound is added only to the second 24-hour soak whose pH is higher. However, the pH of the second soak must be held below 11 or else the stock will shrink when immersed in hot water; thus the reducing potential of the sulfide is less than it would be in the lime system. Experimental data concerning the use of sodium sulfhydrate or sodium sulfide indicate they do not increase the ease of unhairing to a measurable extent when used as soaking assists in the hot-water system.

The relatively mild treatment given skin or hide in the hot-water process never produces the ease of unhairing given by the conventional lime system. Many reagents will cause loosening of hair to some extent, but no set of conditions employed could duplicate the easy unhairing produced by liming.

The nature of the hot-water process limits the range of pH which can be used for soaking. If the stock is soaked initially in a solution of pH greater than 9.5, there is subsequent reduction in the ease of unhairing. If the pH of the second soak is higher than 11.0, the hot-water immersion will swell the stock. A restriction of process duration to 48 hours limits the possible combination of soaking conditions and the amount of rehydration which can take place. This restriction was imposed to place the process on an equal basis, time-wise, with frequently used commercial practices of unhairing.

SUMMARY

Hot-water unhairing of cured calfskin and cattlehide has been accomplished on pieces unhaired by hand in the laboratory. Unhairing of untreated cured stock by this method is not possible without accompanying damage to the grain; however, by soaking the stock for 48 hours in mild alkalis plus a detergent prior to immersion in hot water, unhairing can occur. No experimental conditions produced hair loosening to the same extent that is accomplished in the conventional lime system. The addition of a detergent to the first 24-hour soak enhances hair loosening; other combinations of soaks or immersion bath and detergents did not increase the ease of unhairing. Reducing compounds such as mercaptoethanol, sodium sulfhydrate, and sodium sulfide did not increase the ease of unhairing at the pH conditions of the soaks. Dimethylamine as an additive to the soak liquors did not increase the ease of unhairing. The best results were obtained in a system of 24-hour soaking with 0.1*N* sodium bicarbonate plus 0.05% Detergent A, followed by a 24-hour soaking with 0.1*N* sodium bicarbonate–sodium carbonate buffer. Specimens could then be unhaired after being immersed for 6 minutes in preheated water at 60°C. or for 15 minutes at 55°C. These two conditions of immersion gave similar results and the best results of time-temperature studies for calfskin and cattlehide.

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Received July 11, 1958.

EFFECT OF THE MOISTURE CONTENT OF THE LEATHER ON THE BALL BURST PROPERTIES

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ABSTRACT

Tests were made to determine how the ball burst properties of chrome-tanned upper leather were affected by (*a*) skin position, (*b*) water content of the leather, and (*c*) conditioning of the leather to different moisture contents and then reconditioning in a standard atmosphere.

The results indicate

(*a*) That the properties vary over the skin in a fairly definite pattern.

(*b*) That the bursting strength and the distortion at burst increase as the moisture content of the leather increases, while grain crack load and the distortion at grain crack are practically unaffected.

(*c*) That wetting the leather, or drying it within the limit of these tests and then reconditioning to standard condition, has a measurable effect on the equilibrium water content but little effect on the ball burst properties.

INTRODUCTION

Two separate studies of the effect of the water content of the leather on the ball burst properties were made. The first was designed to study the combined effect of skin position and changes in water content; the second was designed to show the average effect over the whole hide of wetting or drying the leather, then conditioning it to near equilibrium at 23°±2°C. and 50±2% relative humidity.

The apparatus used in the tests on which this paper is based was made before the complete details of ALCA Method E14, "Bursting Strength, Ball" had been settled. The principles of the method are the same, but the apparatus and procedures used in these tests differ in several details from Method E14.

The yoke and specimen clamping device were designed to take advantage of the recording devices of the Instron Machine and to insure that the speci-

men was clamped all around the edge even though its thickness varied to some degree.

The orifice, i.e., the hole through which the leather is pushed, is 7/8″ in diameter and a ball-end plunger 3/8″ in diameter is used in the test kit, whereas a 3/4″-diameter orifice and 1/4″ ball are called for by Method E14. The crosshead speed used in the tests was two inches per minute instead of three inches per minute as required in the ALCA Method.

The detailed variations noted above might have some effect on the absolute values of the data, i.e., it is possible that a higher bursting load might be obtained because of the larger plunger or that greater distortion at burst might be obtained because of the larger orifice used in these tests, but it seems doubtful that such small variations in detail would seriously affect the percentage change in any property due to water content only.

EXPERIMENTAL

Specimens.—A number of skins of finished chrome-tanned shoe upper leather were secured for these and other tests. The skins varied in size from 12 to 14½ square feet and were split all over. The thickness of pieces cut from all parts of six hides varied between the rather narrow limits of 0.033

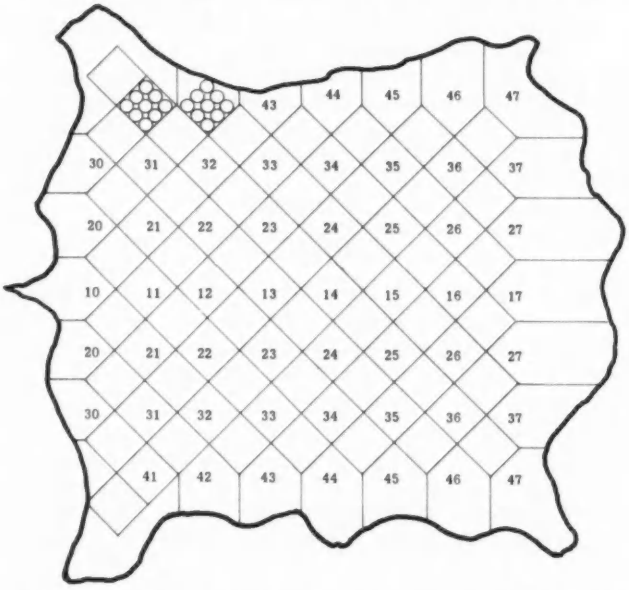

FIGURE 1.—Sampling diagram. 9 disks 1 3/8″ in diameter were cut from each numbered block.

to 0.046 inches when measured with a dead-weight gauge. The leather was of average quality for break, roundness, and general feel, but care was taken to select skins which were free from scars and blemishes. The smallest skin was laid out as shown in Fig. 1. The blocks were 5-3/4″ square and their sides were at 45° to the backbone. In order to keep the centers of each block, such as block No. 25, in the same location on each skin, the size of the blocks was increased with the size of the skin. If the skin was warped out of shape, an attempt was made to locate the blocks as nearly as possible in the proper hide position. No badly warped skins were used. The leather in the unnumbered blocks was cut out first and used for other tests. The skins had been stored at 23°±2°C. and 50±2% relative humidity for several months before the specimens for these tests were cut.

Procedure

Test No. 1.—Nine disks 1-3/8″ in diameter were cut from each numbered block from each of six hides (Fig. 1). Two disks from each block were selected to form a group of specimens. (The extra disk from each block was used in other tests.) Blocks 10 to 17 are along the backbone, so each group for these locations contains only twelve specimens. The other locations have blocks on both sides of the skin, so each group for location 20 to 47 contains 24 specimens. The thickness of each specimen was measured at standard condition with a dead-weight gauge.

One group of specimens was conditioned in each of the following ways:

(*a*) Held at standard condition, i.e., 23°±2°C. and 50±2% relative humidity.

(*b*) Four weeks in a desiccator over $CaCl_2$.

(*c*) Four weeks in a desiccator over H_2O.

(*d*) Soaked in distilled water for three days. The specimens were evacuated at start of the soak.

Specimens were removed one at a time from the conditioning vessel, and weighed and tested immediately. After the tests were completed, the specimens were dried at 105°C. for 48 hours and reweighed to determine their water content.

Test No. 2.—A single skin was taken from the same group of skins as those used in test No. 1. Nine disks 1-3/8″ in diameter were cut from each numbered block (Fig. 1). One specimen from each block, 54 specimens in all, was used to form a group. One group of specimens was treated in each of the following ways:

(*a*) Kept at standard condition, 23°±2°C. and 50±2% relative humidity.

(*b*) Four weeks in a desiccator over $CaCl_2$ at 23°±2°C.

(*c*) One week in a dry oven at 70°C.

(*d*) Four weeks in a desiccator over a saturated solution of KBr, relative humidity 85%, approximately at 23°±2°C.

(*e*) Four weeks in a desiccator over H_2O at 23°±2°C.

(*f*) Four weeks in a desiccator over $CaCl_2$, then reconditioned at 23°±2°C. and 50±2% relative humidity for three weeks.

(*g*) Dried at 70°C. for one week, then reconditioned at 23°±2°C. and 50±2% relative humidity for three weeks.

(*h*) Four weeks in a desiccator over KBr, then reconditioned at 23°±2°C. and 50±2% relative humidity for three weeks.

(*i*) Four weeks in a desiccator over H_2O, then reconditioned at 23°±2°C. and 50±2% relative humidity for three weeks.

The specimens from (*b*), (*d*), and (*e*) were removed from the conditioning desiccator one at a time, and immediately weighed and tested. The specimens from (*c*) were taken from the drying oven, cooled in a desiccator over

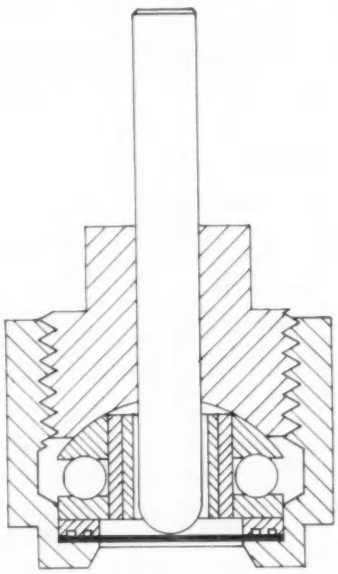

FIGURE 2.—Sectioned drawing of specimen holder.

$CaCl_2$, and then removed one at a time, weighed, and tested. All specimens that were room-conditioned were weighed after testing. All tested specimens were dried at 105°C. for 48 hours and weighed to determine their moisture content.

Testing.—All tests were made on an Instron Tensile Testing Machine. This is an autographic machine which can be arranged to plot a load-crosshead displacement curve. There is a pip button on the machine which can be pressed at any time to give the curve-plotting stylus a sharp but small deflection. If the pip button is pushed at the instant the grain cracks, the load displacement curve is marked, and both the load and the distortion of the leather diaphragm at grain crack can be read from the load displacement curve. The load required to cause bursting and the deflection of the diaphragm at the time of burst can also be read from the curve.

The design of the specimen holder and test plunger is shown in the sectioned drawing, Fig. 2. The specimen is shown as a shaded band just under the tip of the ball-end plunger. The specimen clamp is a grooved washer. The grooves help to keep the specimen from slipping when the load is applied.

The balls and spherical washer above them represent a self-aligning ball thrust bearing. When the nut is screwed down on the clamping washer, the self-aligning bearing insures that the specimen is clamped on all edges even when the thickness of the specimen varies around the edge. The balls allow the nut to turn freely without tending to twist the clamping washer on the specimen.

As noted above, the hole through which the specimen is pushed is 7/8″ in diameter and the plunger is 3/8″ in diameter with a ground ball end.

Figure 3 is a photograph of the yoke which holds the test fixture, mounted in the machine. A bracket, mounted on the crosshead which holds the test fixture, carries a mirror tilted at 45° to the vertical in which the bottom of the specimen can be lighted and viewed during the test. In the photograph the ball end of the plunger can be seen, reflected in the mirror, just as it bursts through the specimen.

A machine crosshead speed of 2 inches per minute was used and the load crosshead displacement chart was run at 10 inches per minute, so the distortion of the leather diaphragm was multiplied by a factor of 5, making the reading of the distortion values more accurate.

The bottom of the specimen was observed in the mirror during the test, and when the grain cracked, the pip button, mentioned above, was pressed to record the load and distortion.

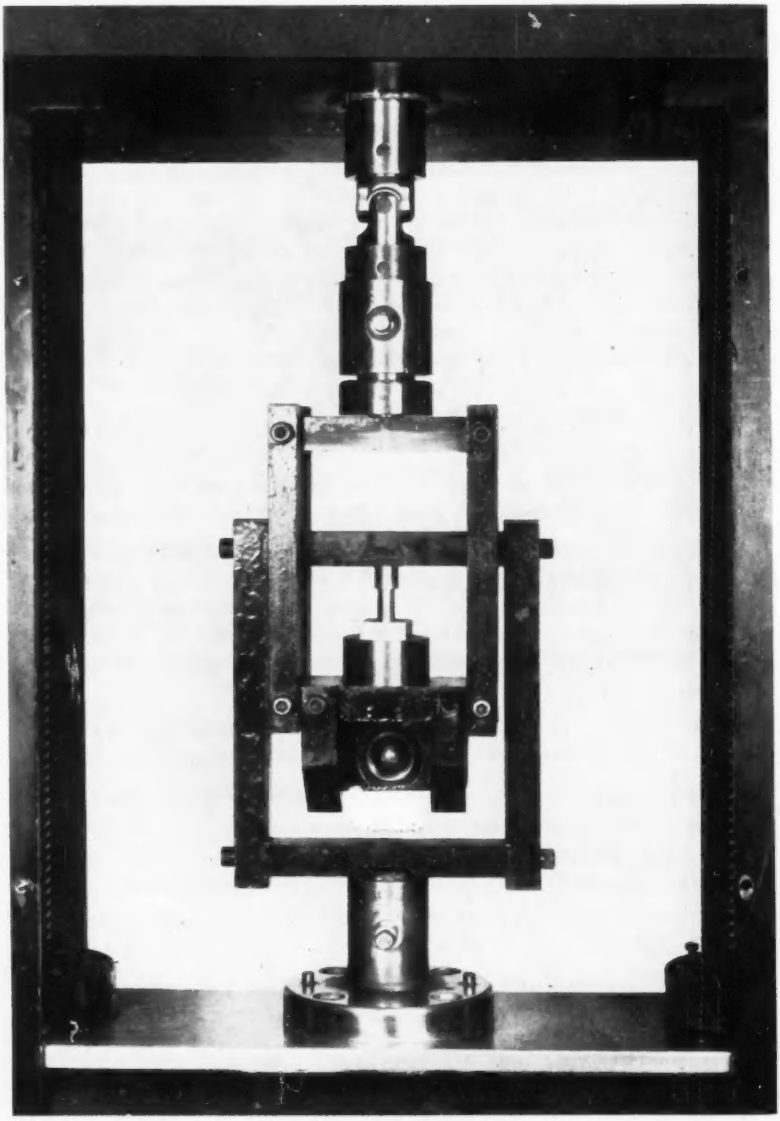

FIGURE 3.—Yoke which holds the test fixture. The ball end of the plunger can be seen in the mirror just as it bursts through the specimen.

RESULTS

After the tests were completed, the following values were read from the load-distortion chart: (*a*) the load and distortion at grain crack, (*b*) the load and distortions at burst, (*c*) the distortion between 10 and 50 lb. of load, and (*d*) the distortion between 50 and 100 lb. of load.

The loads at grain crack and at burst were recorded and plotted as "Grain Crack Load" and "Bursting Load" respectively. The loads were not corrected for thickness except as noted below.

The distortion between 10 lb. and 50 lb. of load and that between 50 lb. and 100 lb. were used to calculate two values which will be designated as Moduli of Distortion and represented in the tables by M_1 and M_2.

Thus, if D_1 is the distortion caused by raising the load from 10 lb. to 50 lb., and D_2 is the added distortion caused by raising the load from 50 lb. to 100 lb.,

$$\text{then } M_1 = \frac{50\text{–}10}{D_1} = \frac{40}{D_1}$$

$$\text{and } M_2 = \frac{100\text{–}50}{D_2} = \frac{50}{D_2}$$

The results are plotted wherever possible (Figs. 4–15).

The hide plans at the bottom of Fig. 4 show the hide locations of the blocks from which the specimens that were used to obtain the plotted values were cut. The abscissae of Figs. 5–8, 11, and 12 were laid out in the same way as that of Fig. 4, but the hide diagrams have been omitted.

The group of points near the center of the curves of Figs. 13–15 are for the leathers which were first conditioned in an atmosphere other than standard and then reconditioned in the standard atmosphere.

The results indicate:

1. Effect of Skin Position
   a. The bursting load varied over the skin according to a definite pattern (Fig. 4). Some skins are stronger at all locations than others but the pattern of variation is very closely the same for each separate skin (Fig. 5).
   b. The grain crack load (Fig. 6) varied over the skin according to a pattern quite similar to that for the bursting load (Fig. 4).
   c. The distortion at burst was not significantly different at various skin positions (Fig. 7).
   d. The distortion at grain crack was not significantly different at various parts of the hide (Fig. 8).

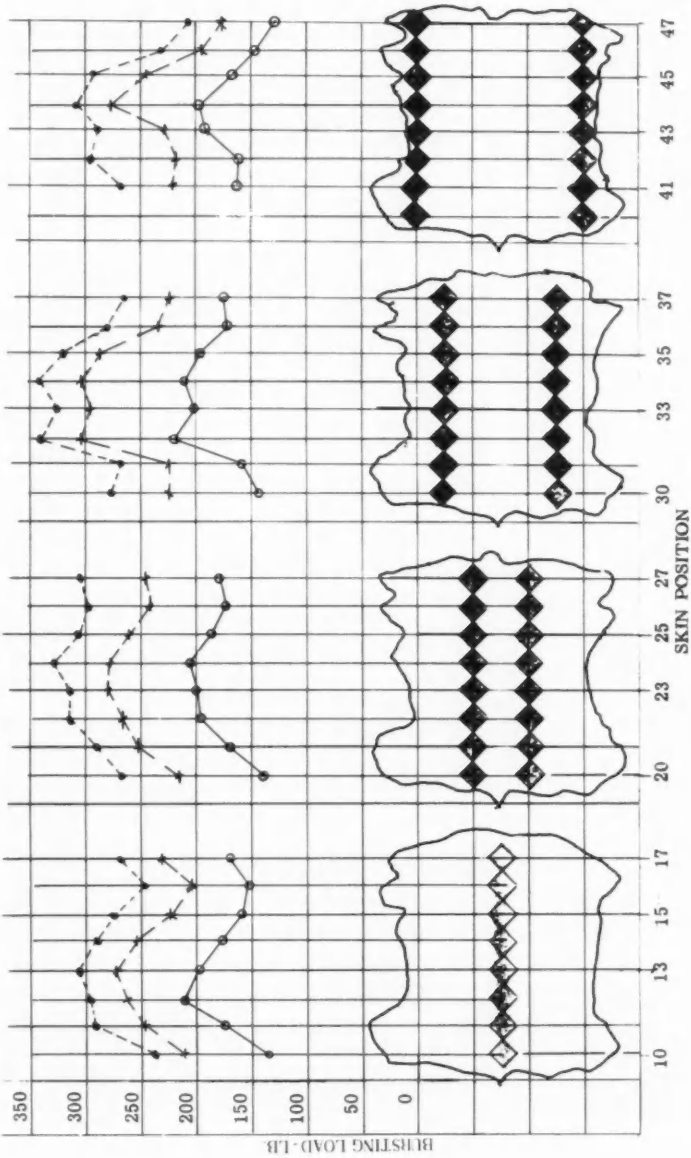

FIGURE 4.—Bursting load as a function of water content and skin position.
Water contents: ● 42% × 20% ○ 3%.

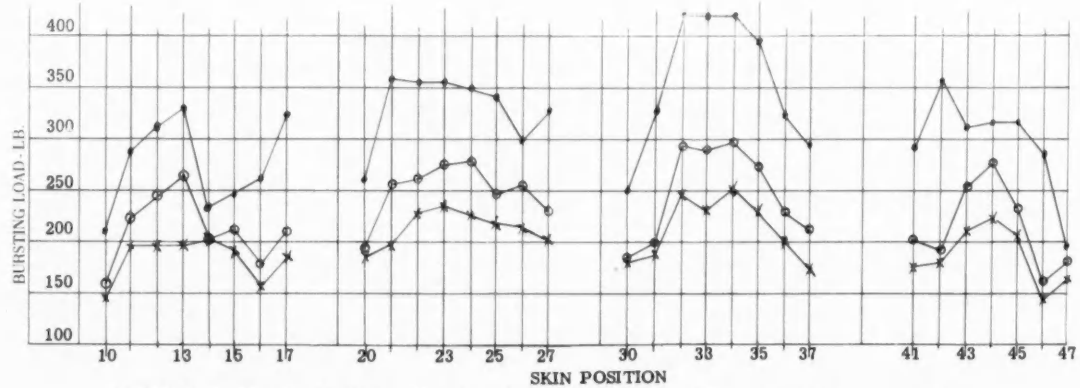

FIGURE 5.—Bursting loads as a function of skin position for individual skins at room condition.
● strongest ○ median × weakest skin.

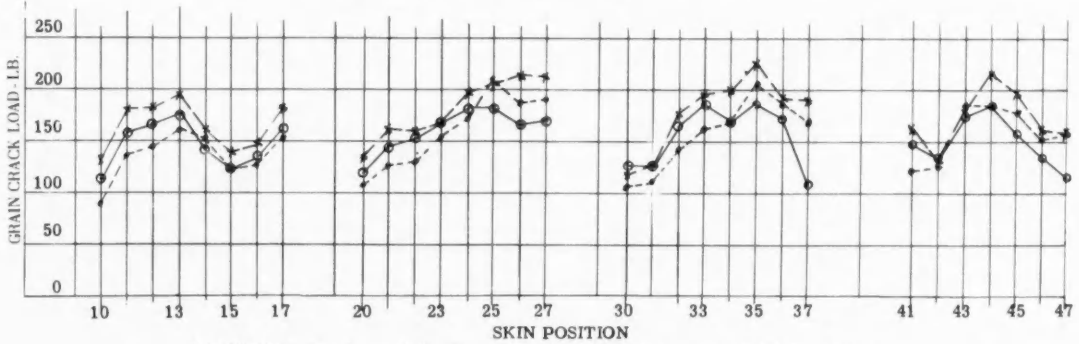

FIGURE 6.—Grain crack load as a function of water content and skin position.
Water contents: ● 42% × 20% ○ 3%

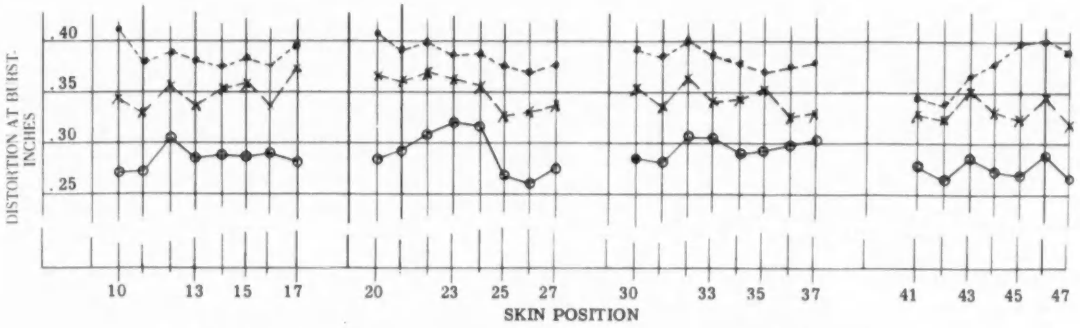

FIGURE 7.—Distortion at burst as a function of water content and skin position.
Water contents: ● 42% × 20% ○ 3%

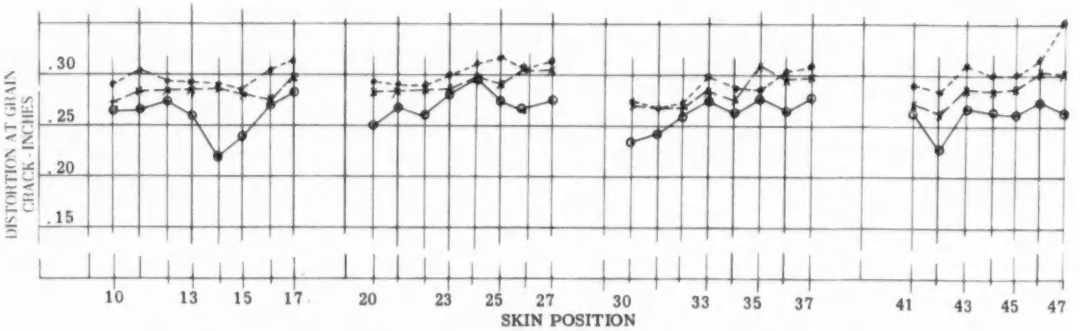

FIGURE 8.—Distortion at grain crack as a function of water content and skin position.
Water contents: ● 42% × 20% ○ 3%

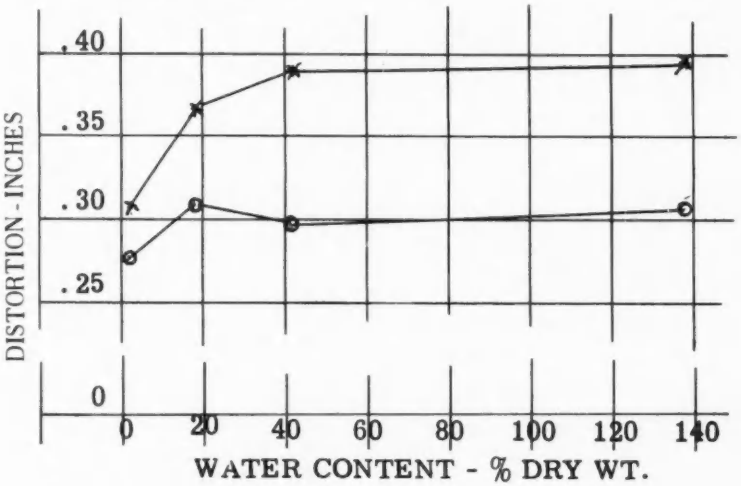

FIGURE 9.—Distortion at grain crack and at burst as functions of water content.

× burst ○ grain crack

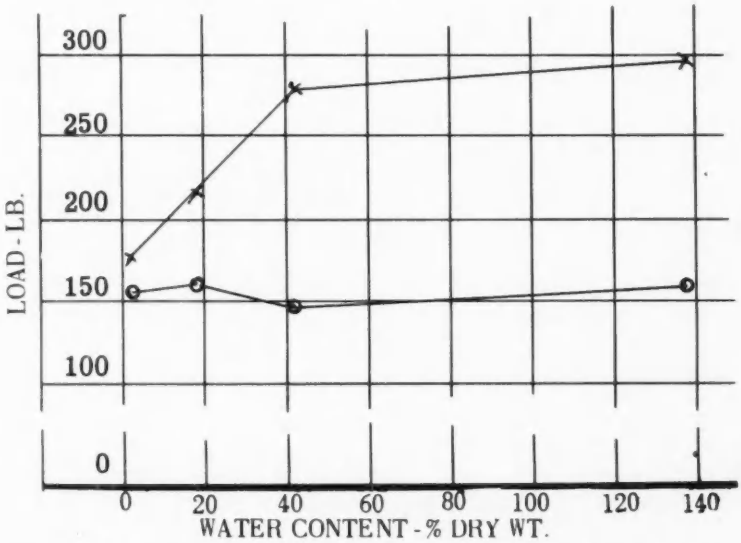

FIGURE 10.—Grain crack load and bursting load as functions of water content.

× burst ○ grain crack

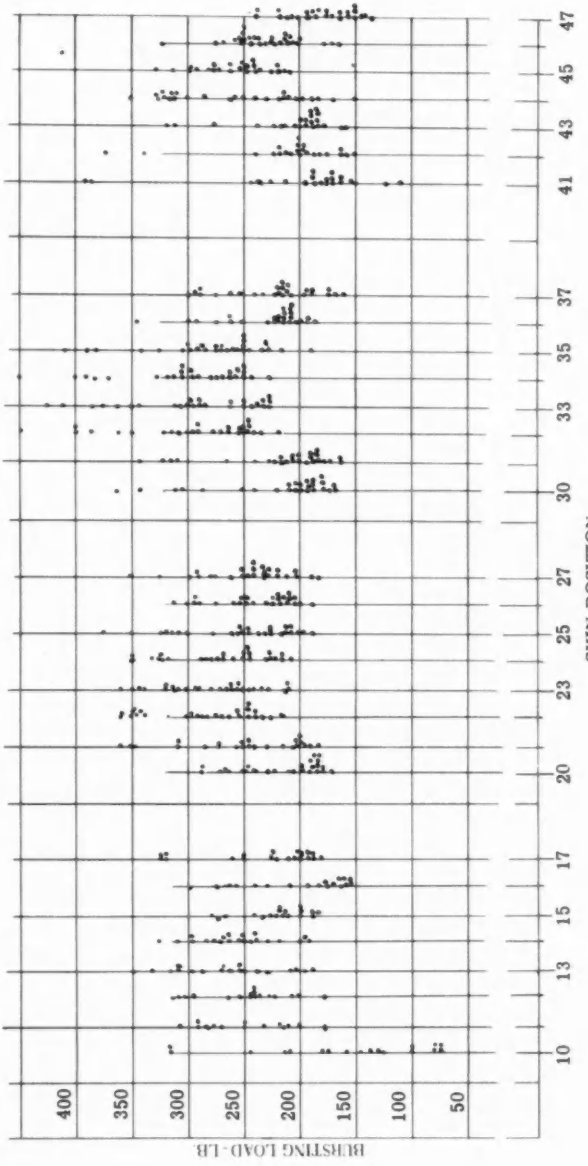

FIGURE 11.—Scatter diagram of bursting load as a function of skin position for 6 individual skins at room condition.

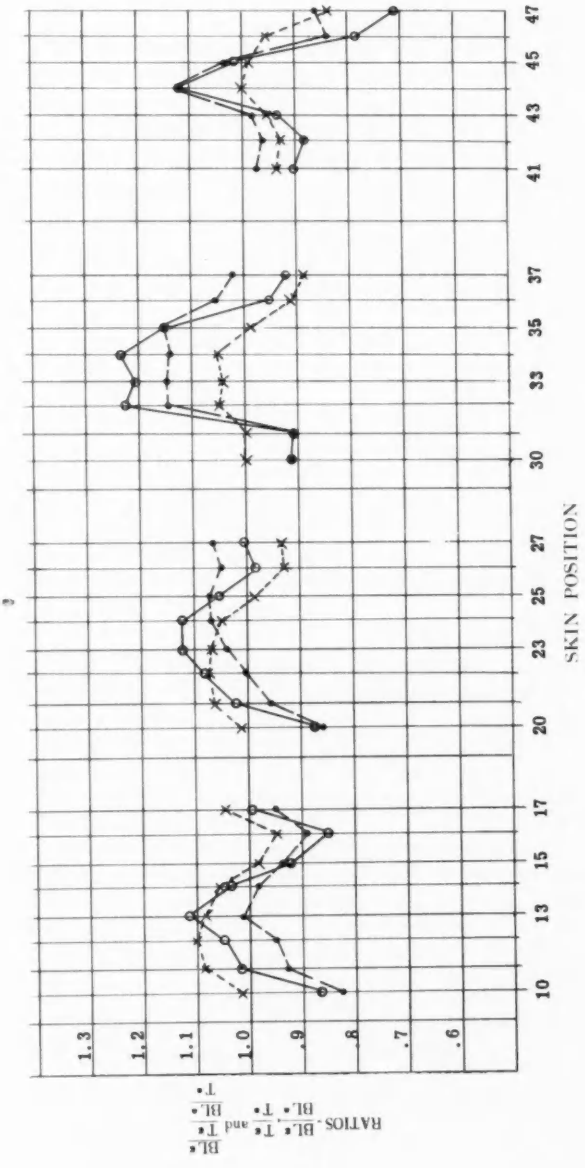

FIGURE 12.—Ratio of position average to skin average as a function of skin position for: ○ bursting load, × thickness, and ● bursting load divided by thickness.

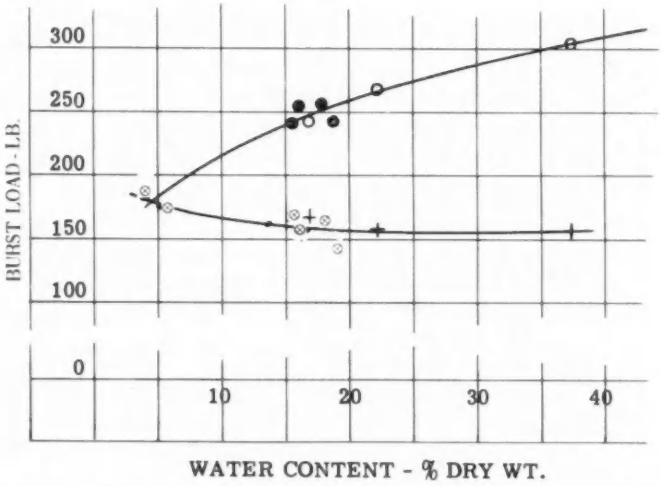

FIGURE 13.—Effect of conditioning and reconditioning on burst load and grain crack as functions of water content.

○ burst load
● burst load, reconditioned
+ grain crack load
⊗ grain crack load, reconditioned

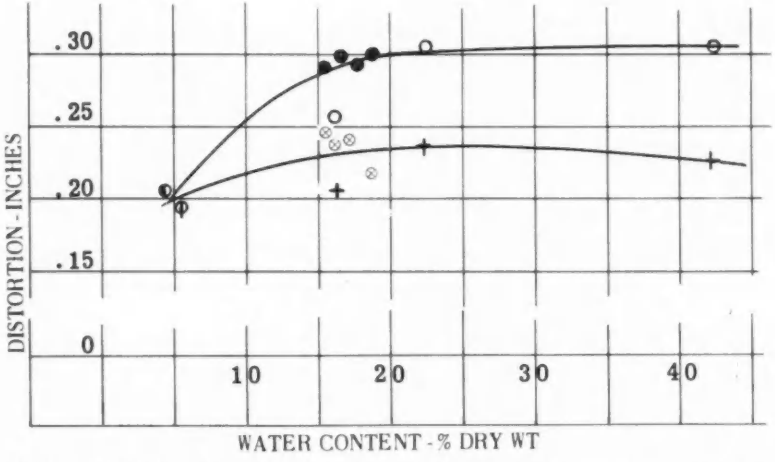

FIGURE 14.—Effect of conditioning and reconditioning on distortion at burst and at grain crack as functions of water content.

○ distortion at burst
● distortion at burst, reconditioned
+ distortion at grain crack
⊗ distortion at grain crack, reconditioned

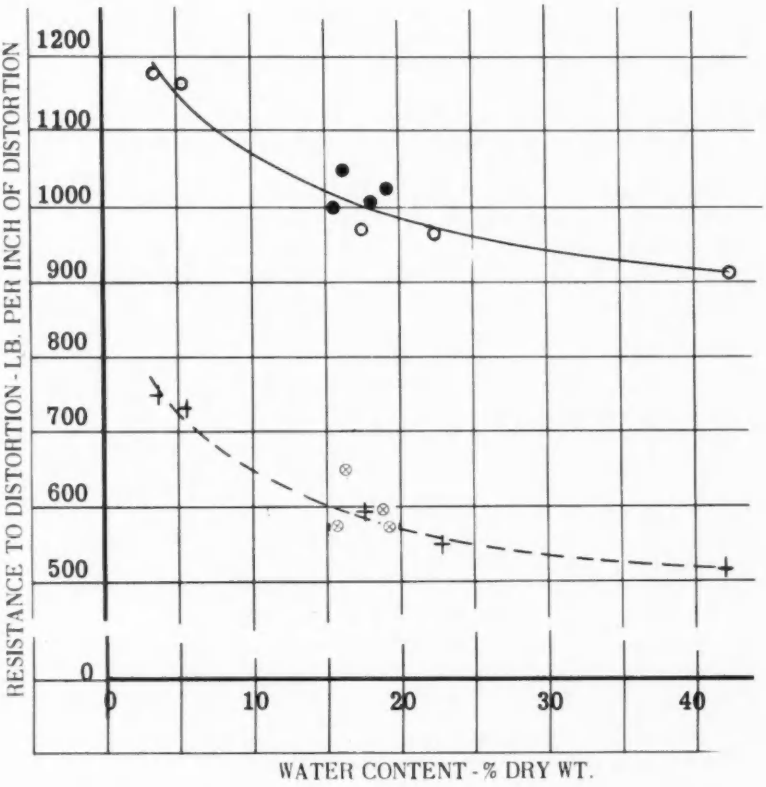

FIGURE 15.—Effect of conditioning and reconditioning on modulus of distortion as a function of water content.

○ 50- to 100-lb. loads
● 50- to 100-lb. loads, reconditioned
+ 10- to 50-lb. loads
⊗ 10- to 50-lb. loads, reconditioned

2. Effect of Water Content

Note: The water content of the leather used in these tests seemed high, so pieces of the test leather and pieces of other chrome-tanned upper leathers were conditioned and dried together under each of the conditions used in the test. The leathers used in this test had approximately 5% higher water content than the other leathers after storage at standard condition, over a saturated solution of KBr, and over water, but they had

equal water content when stored over $CaCl_2$ and dried at 70°C. The reason for the higher water content was not determined.

a. The bursting load increased with increasing water content up to 42% (Fig. 4), then increased only slightly more as the water content was raised to 135% (Fig. 9).
b. The grain crack load is practically unaffected by the water content of the leather (Figs. 6 and 9).
c. The distortion at burst increased significantly as the water content was raised from 3% to 42% (Fig. 7), but there was only a slight further increase as the water content was raised to 135% (Fig. 10).
d. The distortion at grain crack increased only slightly with increased water content (Figs. 8 and 10).
e. The average modulus of distortion, i.e., the pounds force per inch of distortion taken between 10 lb. and 50 lb. of load, varies only slightly with changes in the water content (Table I). The reversing trend shown in that table probably has no significance.

TABLE I

AVERAGE MODULUS OF DISTORTION

Water Content	Distortion in inches at 10 lb.	50 lb.	Modulus $40\phi/D$*
3%	0.051	0.125	590
19%	0.057	0.123	607
42%	0.061	0.138	520

*D is the distortion produced by increasing the load from 10 lb. to 50 lb.

3. Variability

a. The range of the variations between individual specimens at each skin location is best shown by a scatter diagram (Fig. 11). At each hide position, at least the top three points came from one skin which was considerably stronger than any of the other five.
b. The range of the variations between skins is shown in Fig. 5 where the data for the strongest, the weakest, and the median skins are plotted.

4. Effect of Thickness

To determine whether or not changes in thickness could account for the differences in strength indicated at various parts of the skin, the following procedure was followed:

The average value of the bursting load, BLa, and the average value of the thickness, Ta, for all the specimens from all skin locations used in test No. 1 and held at standard condition were determined. This gave an average value of the bursting load and an average thickness for the full hide. The average value of the bursting load, BLg, and the average value of the thickness, Tg, for the group of specimens cut from each hide location were also determined.

The position values of the bursting strength were divided by the value for the skin, i.e., $\frac{BLg}{BLa}$, giving a ratio at each skin position which varies from one skin location to another in the same way as the bursting strength itself, but the reference value is made 1 instead of 0. These values are plotted on Fig. 12 as circles connected with solid lines.

Thickness ratios, $\frac{Tg,}{Ta}$ were found for each skin location. These results are plotted on Fig. 12 as crosses connected with dotted lines and show how the thickness varies over the skin.

To determine how the bursting load is affected by the thickness, the average bursting strength, BLa, was divided by the average thickness value, Ta, to give an over-all skin value of the ratio $\frac{\text{bursting load}}{\text{thickness}} = \frac{BLa}{Ta}$. A similar factor, $\frac{BLg}{Tg}$, was determined for each skin position. The ratio of $\frac{\frac{BLg}{Tg}}{\frac{BLa}{Ta}}$ was then determined for each

TABLE II

Treatment	H_2O %	Load (lb.) Burst	Load (lb.) Grain Crack	Deflection Burst	Deflection Grain Crack	M_1*	M_5†
a	17.5	234	166	0.300	0.244	595	973
b	5.2	171	171	0.190	0.190	735	1165
c	3.1	178	178	0.201	0.201	742	1176
d	42.3	312	162	0.308	0.225	570	1110
e	22.7	286	170	0.298	0.226	554	967
f	16.2	252	165	0.256	0.204	656	1050
g	15.2	242	172	0.291	0.247	578	1000
h	19.2	245	143	0.300	0.226	583	1035
i	18.3	255	168	0.296	0.246	594	1020

*M_1 is the Modulus of Distortion between 10 and 50 lb.
†M_5 is the Modulus of Distortion between 50 and 100 lb.

skin position. These values are plotted on Fig. 12 as solid dots connected with broken lines and show how the thickness affects the bursting load at each skin location.

The plots show that the skins tend to be thick where the bursting strength is high and thin where the strength is low. The curve for the bursting load divided by the thickness tends to have the same shape as the other curves. The changes in thickness found in these skins, therefore, account for only part of the variation in the bursting load, and the variations in load at different hide positions indicate real differences in the strength of the leather.

5. Effect of Reconditioning—Test No. 2

   a. The moisture content of the leather at the time of test has a marked effect on the ball burst properties (Table II and Figs. 13–15).

   b. Wetting or drying of the leather, then reconditioning at standard conditions, has a small but consistent and measurable effect on the moisture content of the leather, but the ball burst properties are not greatly affected (Table II and Figs. 13–15).

SUMMARY

The plots of the data for test No. 1 show the existence of a definite pattern of variation in the ball burst properties over the skin. The pattern of variation is the same for each individual skin and at all moisture contents, even though the leather in some skins is stronger than in others, and wet skins are stronger than dry.

Table II shows that when leather is given a preliminary treatment, i.e., either wet or dried before reconditioning in a standard atmosphere, the equilibrium moisture content at standard condition is affected by 1% to 2%. The leather which was dried regains a lower moisture content than the leather which was moistened. The difference in the equilibrium moisture content is not great, and the ball burst properties at standard condition are not significantly affected.

Received July 28, 1958.

LIFE LINES

Brief Biographies of Our Contributors

RAYMOND HAUCK was graduated from Miami University (Ohio) in 1950. After two years as a statistical analyst with the General Electric Company, he joined the Tanners' Council Research Laboratory as a research associate. In 1957 he received the degree of M.S. in Leather Chemistry at the University of Cincinnati.

MIETH MAESER—See the March 1958 *Journal*.

Manufacture of Calf Kid in Philadelphia. Choice skins only can be used. From 6 to 10 pounds is the most suitable weight, although some manufacturers turning out a heavier article use skins weighing as much as 18 pounds. The skins, whether green or salted, are soaked, according to the season of the year, for 12 or 14 hours, a few hours more in winter and less in summer, this depending entirely on the condition of the skins and the temperature of the water. They are then "stretched", when they are again soaked for 1 to 2 hours, and are then ready for liming. The skins, as a general rule, are first placed in old lime for at least 1 to 2 days, and then in fresh lime for about 6 days. For preparing the fresh lime-bath 3 bushels of lime are taken to 12 dozen of skins. The skins, when coming from the lime-bath, are depilated and thrown into fresh water in order to wash out the lime. They are then fleshed. The well-known ooze, consisting of dog dung mixed with pigeon dung, is then prepared. Opinions differ as regards the quantity of ooze to be used, every manufacturer being guided by his own experience and judgment. The skins remain in the ooze from 30 minutes to 2 hours, when they are smoothed and then thrown into a mixture of bran and water, where they remain for 24 hours. They are then taken out, washed and cleansed from all adhering particles of bran, and scraped. The skins are now ready for the aluming. For a dozen skins take 2½ pounds of alum, about 13 to 14 ounces of salt, the yelks of 24 eggs, and 2½ pounds of flour; mix all thoroughly together, throw the skins into the mixture, and let them lie in it over night. They are then hung up to dry in the air, after which they are stretched and pared down to the desired thickness. They are again dried in the air to prepare them for the second bath, consisting of eggs and salt, and again stretched, when they are ready for dyeing. This is done with a preparation of a bichromate salt, urine, logwood, and sulphuric acid. They are again hung up and dried, smoothed, and finally ironed, after which they are oiled with prepared neats-foot oil and rubbed with caoutchouc to remove the oil, which finishes the work, 4 to 6 weeks being required to prepare such a skin.

—*The Techno-Chemical Receipt Book*. Philadelphia: Henry Carey Baird & Co., 1903.

New Process of Depilating Hides. The hides are placed in a solution prepared by mixing together dilute solutions of ammonia and sulphurous acid. Woolly hides are coated on the flesh side with a dough made of potter's clay and the above mixture. In place of ammonia the salts of ammonia may be used.

—*The Techno-Chemical Receipt Book*. Philadelphia: Henry Carey Baird & Co., 1903.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

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Ian C. Somerville, Rohm & Haas Company, 5000 North Richmond St., Philadelphia 37, Pennsylvania

C. David Wilson, Fred Rueping Leather Company, Fond du Lac, Wisconsin

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Notice to Authors

Authors are requested to introduce each paper submitted to the *Journal* by an abstract of the article. Articles should also be accompanied by a brief biography of the author(s) for inclusion in the "Life Lines" feature in the *Journal*. Unnecessary correspondence will also be avoided if a notation is attached to the copy indicating where the author desires galley proofs to be sent.

To

PROFESSOR ADOLF KÜNTZEL

Director of the Institute of Leather Chemistry

Technical High School, Darmstadt, Germany

founder and Editor of *Das Leder*

distinguished contributor to the science of

leather manufacture

and warmhearted humanitarian

the leather chemists of America

offer heartiest congratulations and best wishes

on the occasion of his sixtieth birthday.

REPORT OF MINERAL LEATHERS COMMITTEE

The Mineral Leathers Committee met on May 25, 1958, at the New Ocean House, Swampscott, Massachusetts. In attendance were N. C. Benrud, S. B. Foot Tanning Co., chairman; Robert Adams, B. D. Eisendrath Tanning Co.; T. S. Perrin, Diamond Alkali Co.; Ludwig Seligsberger, Quartermaster Research and Development Center; Robert Stubbings, Lehigh University, and William T. Roddy representing Dr. O'Flaherty, Tanners' Council Laboratory, University of Cincinnati. Visitors were Mieth Maeser and J. R. Kanagy.

In reviewing the Methods of Analysis the committee voted that the last sentence under Section C1, 4.1.1 should be deleted. This sentence reads: "The nitric acid may be omitted from the oxidizing mixture". Nitric acid is necessary in wet oxidation of leather and the danger of explosion would be present if someone unfamiliar with the use of perchloric acid misunderstood the above statement.

The committee also voted against the revision of Section D10, 4, Procedure, 4.1 Wet oxidation, dated December 31, 1956, and favored the original ALCA provisional method of May 1954. The change was in the method of adding the acids to oxidize the organic matters and the trivalent chromium. No one present knew of a reason for the change. It had not passed through the mineral analysis group, according to the previous chairman, Mr. Adams.

The group also noted and wishes to call to the attention of Council that there is a duplication of the method for the determination of pH on leather. These are B20 and D35 under Vegetable and Chrome leathers.

The committee discussed and then voted to take no action on the determination of zirconium compounds fillers in leather since there has been no request for the inclusion of such determinations in the methods book.

The final work on the determination of chromic oxide and the Lehigh Overall Basicity and a preliminary report on this work, were discussed. Several changes in the report were requested. These are to be made by the chairman and the report presented for publishing.

N. C. BENRUD, *Chairman*

PAPERS FOR SIXTH BIENNIAL CONFERENCE OF THE INTERNATIONAL UNION OF LEATHER CHEMISTS' SOCIETIES—MUNICH, SEPT. 6–12, 1959

Any member who wishes to submit a paper for presentation at the Munich Conference, Sept. 6–12, 1959, must submit the *full text* of the paper to the Honorary Secretary of the International Union, Mr. G. Forsyth, Highfield Tanning Company, Runcorn, England, by May 1, 1959. This will enable the Executive Committee of the International Union to select suitable papers, provide for their translation, and arrange the program.

Members who wish to enter papers in the prize competition announced in the August 1958 number of *JALCA* are reminded that all such papers must reach the Editor-in-Chief of this journal not later than March 1, 1959. For details, see page 474 of the August number.

COUNCIL MEETING

October 14, 1958

Sheraton Hotel
Philadelphia, Pennsylvania

The meeting was called to order by President Maeser at 9:00 A.M. with all of Council present except C. David Wilson who asked to be excused because of important matters in Fond du Lac. Also present were Messrs. Wederbrand, Stubbings, Merrill, Klimpl, and O'Flaherty.

Technical Committee reports.—President-Elect Henrich advised that he had not received reports from all committees, but that he would have a complete composite report for the January meeting of Council.

Dr. Henrich also advised that the Method of Bleed Resistance had not been printed with the other methods but was published later and sent to all members. He advised that an error in the Glucose Determination Method has been noted and a correction published in the *Journal.*

Dr. Henrich reported that E. B. Thorstensen, Chairman of the Tannery Effluents Committee, had recommended the following members to serve on his committee: Theodore Braunschweig, Jack Wagoner, Joseph Naghski, F. Leslie Collins, and Edward Botan. Upon motion by Clinton Retzsch, seconded by Charles Martin, Council unanimously approved this committee.

Dr. Henrich reported that Dr. T. Thorstensen had requested that the following persons be added to his Raw Stock Committee: Thomas Dorrian, Edward Mellon, J. M. Cassel, and G. M. Oliensis. These additions were unanimously approved by Council.

The question arose regarding the Subcommittee on Zirconium; it was reported that they were preparing a report.

Editor's report.—Dr. Henry Merrill reported that he had manuscripts of eleven accepted papers and that about five more were out to the Editorial Board. This should carry the *Journal* nicely to March. Also there were four papers presented at the last meeting which have not yet been submitted.

The matter of using colored illustrations with papers in the *Journal* was discussed. Council decided that if the author or his company would agree to pay the difference in cost of printing between color and black-and-white, then such colored illustrations could be used. This then will become the policy.

New Editor-in-Chief.—The committee, consisting of Harold Miller and Clinton Retzsch, appointed to recommend a successor to Dr. Merrill at the expiration of his tenure of office made their report and recommended Dr. Wallace Windus who has agreed to accept such appointment. Council unanimously approved the report.

In the discussion it was the consensus of Council that the new Editor should have the freedom of reorganization and of appointing his assistants and Editorial Board.

Upon a motion made, seconded, and unanimously carried, Council approved the appointment of Dr. Wallace Windus as Editor-in-Chief to succeed Dr. Henry B. Merrill on March 1, 1959. President Maeser is to discuss the above matters with Dr. Windus so that he can make his plans and present them at the January meeting of Council.

Ways and Means Committee.—Mr. Wederbrand reported that the Association was operating within the allotted budget of 1958. He also reported that a net gain had been secured in advertising revenue.

There was much discussion regarding those firms who provide their products to the Industry but who do not advertise. Upon a motion made, seconded, and unanimously carried, it was agreed that Messrs. Wederbrand and Retzsch would prepare a letter to be sent to every member asking their aid in the matter.

Convention.—Dr. Stubbings reported that he had secured the following committee to serve: Fred Klimpl, Associate Chairman; Arthur Carlson and W. B. Hartnett, Golf; W. A. Wachholtz, Transportation; and Mrs. Arthur Carlson, Women's Activities. Dr. Stubbings is still to obtain some one on Publicity. This Committee was approved by Council.

It was agreed by Council that the matter of display booths at Mackinac is to be in the hands of Mr. Wederbrand who will clearly advise all prospective sponsors of the conditions.

The Convention Committee will submit a detailed budget at the January meeting.

Council reaffirmed its commitment to go to Lake Placid Club in 1960.

Committee to Develop Method of Determining Hide Substance Nitrogen from Added Materials Containing Nitrogen.—After much discussion it was agreed that this matter might be referred to the several committees concerned and have them collectively prepare a statement for publication in our Methods Booklet, which will advise of the inadequacy or limitation of the present method for determining hide substance nitrogen, i.e., to differentiate HS nitrogen from added materials which would analyse as part of the total nitrogen. Upon a motion duly made and seconded, Council unanimously approved the above action.

Symposium.—Council has agreed to continue having the Leathermaking Symposium at the annual meeting following as far as practical the format and policies followed in 1958. After listing a number of possible candidates for chairman of the symposium in 1959, the President was authorized to contact such persons.

Deadline on papers for presentation at the Sixth Congress of the I.U.L.T.C., September, 1959.—As announced in the August, 1958, number of the *Journal*, March 1, 1959 is the deadline for submission of papers by candidates who desire to compete for the $1,000 prize offered to the author of the best paper, for the purpose of defraying his expenses in attending the Munich meeting of the I.U.L.T.C. All such papers should be sent to the Editor-in-Chief of the *Journal*, who will turn them over to the judging committee.

May 1 is the deadline for submitting all papers for presentation at the Munich meeting. All such papers, other than the prize-winning paper, must be submitted in final form to the Honorary-Secretary of the International Union of Leather Chemists Societies.

President to represent ALCA at International Meeting.—Upon a motion by Mr. Martin, seconded by Mr. Miller, and unanimously carried, Council approved the recommendation of the committee appointed to consider this matter, authorized the President to represent ALCA at the Munich meeting, and voted $1,000. towards his expenses.

Convention sites.—Poland Springs House—Mr. Wederbrand reported favorably upon this place for a meeting in 1963. President Maeser is to visit it and report in June.

French Lick, Indiana—The hotel has agreed to hold June 17–20, 1962 until July 1, 1959. This will be decided at the 1959 meeting.

Swampscott, Massachusetts—The New Ocean House is holding dates for us in 1963. Dr. Stubbings is to write them regarding this as they will hold it until July 1, 1959.

Council advised the Convention Committee not to consider such places as Florida but to be alert to any places in the presently patronized states.

Badges.—Council instructed the Secretary to provide leather badges at a cost not to exceed the cost of present plastic badges.

Mutual membership.—A letter from the Indian Leather Technologists' Association was read requesting mutual membership arrangement. Council agreed to do this and furnish the *Journal* at three-fourths the cost now charged to members. It was also Council's decision that all mutual memberships shall pay this same rate.

Draft from British Standards Institution.—All such comments are to be reviewed by President-Elect Henrich and given to President Maeser who will present them to the British during the Munich conference.

New members.—President Maeser reported that he had written to all non-members attending the 1958 meeting and had obtained five new members.

Council meeting.—The next meeting will be on the Friday preceding the January meeting of the Wisconsin Tanners Production Club.

Adjourned.—There being no further business the meeting was adjourned at 3:00 P.M.

Respectfully submitted,
FRED O'FLAHERTY
Secretary

PATENTS

Coated Paper and Leather. Brit. Pat. 795,135. General Aniline & Film Corp. Appl. Oct. 31, 1955.—Paper or leather is coated with the water-insoluble reaction product of a polymeric N-vinyl lactam and a polymeric compound containing free carboxyl groups by applying an aqueous dispersion or an organic solvent solution of the reaction product to the sheet material. The lactam may be a polymer of 1-vinyl-2-pyrrolidine, 1-vinyl-5-methyl-2-pyrrolidine, 1-vinyl-2-piperidone, or N-vinyl epsilon caprolactam. The polymeric compound may be cellulose glycollic acid, alkyds containing free carboxyl groups, polyvinyl alcohol esterified with maleic or fumaric acid, polyacrylic acid, polymethacrylic acid, poly-alpha-chloroacrylic acid, copolymers of these acids, and maleic acid copolymers.

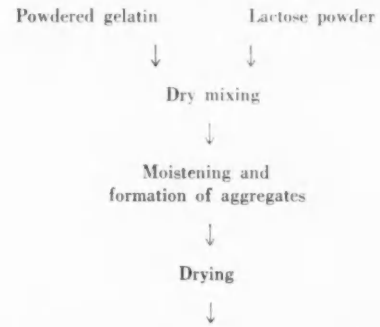
Leather Finishing Resins. Brit. Pat. 795,711. Imperial Chemical Industries, Ltd. Appl. March 1, 1957.—Leather is finished by treatment with an aqueous dispersion of a copolymer or an ester of acrylic or methacrylic acid and a minor amount of an amide, and subsequently with formaldehyde. Specified esters are methyl, ethyl, butyl and β-ethoxyethyl. Specified amides are acrylamide, methacrylamide, casein and gelatin. The amide preferably amounts to from 5 per cent to 20 per cent of the total monomer weight. Examples describe the preparation (Group IV (a)) and use of aqueous dispersions of (1) 95:5 and (2) 92.5:7.5 β-ethoxyethyl methacrylate: methacrylamide copolymers and (3) a β-ethoxyethyl methacrylate:methacrylamide graft copolymer. The finish is applied by padding and/or spraying and fixed by spraying the damp leather with an aqueous solution of formaldehyde. Formaldehyde-liberating compounds such as paraformaldehyde, phenol-formaldehyde, urea-formaldehyde or melamine-formaldehyde resins may be used instead of formaldehyde. The dried leather may be plated or embossed and may be coated with a nitrocellulose lacquer.

Hardening Leather. Brit. Pat. 795,278. Poly-Resin Products, Ltd. Appl. Sept. 13, 1956.—Leather is hardened by impregnation with a solution of *p*H 3–5.5 of a resole type phenol-formaldehyde resin which is preferably condensed so far that the viscosity of a 59± 1 per cent by weight solution in ethyl alcohol is 200–400 centipoises at 25°C. The resin may be prepared from an hydroxy benzene or substituted hydroxy benzene or mixture thereof and formaldehyde; the solvent may be an alcohol, ketone, ester, hydrocarbon, water or mixture of these; the *p*H may be adjusted with formic acid or paratoluene sulphonic acid or mixtures of these. Curing results from the natural acidity of the leather without heating or the addition of accelerators. In Example 1, the resin solution is prepared by condensing one mol. of phenol with two mols. of formaldehyde in an aqueous medium, adjusting the *p*H to 8.5–9 and refluxing at 97°C. for 40 minutes followed by dehydration under vacuum at below 65°C. until a sample of the resin solution resulting dissolved in industrial ethyl alcohol to a concentration of 59± 1 per cent by weight yields a solution of viscosity 200–400

centipoises at 25°C. This resin is then diluted with industrial ethyl alcohol to a resin concentration of 60 per cent by weight and formic acid added to give a *p*H of 4.5. The solution is used to harden parts of footwear by brushing one or more coats on the underside of the leather. In Example 2 a resin prepared as in Example 1 is dissolved in industrial ethyl alcohol and the *p*H adjusted to 3.5 by adding a mixture of equal parts of formic acid and paratoluene sulphonic acid and the resin concentration adjusted to 30± 1 per cent by weight with a viscosity of less than 10 centipoises. The solution is applied in the same manner as in Example 1.

Bating Leather. Brit. Pat. 795,850. Rohm & Haas Ges. Appl. Oct. 22, 1956. —Green or soaked hides or skins which have been fleeced or dehaired by the application of enzymic material in the form of a powder as disclosed in the parent Specification are subsequently enzymically bated at a *p*H of 3–5. Proteolytic enzymes such as pancreatic tryptase, bacterial proteases, or preferably mould fungi tryptases may be employed. By bating at such an acid *p*H the creation of loose grain produced by proteolytic enzymes acting at an alkaline *p*H is avoided. The bating lasts from 6 to 36 hours and if necessary may be preceded by a weak enzymic bating at an alkaline *p*H. In addition to the proteolytic enzymes, mould fungi carbohydrases and/or lipases and advantageously one or more neutral salts such as sodium chloride, ammonium sulphate, or sodium tripolyphosphate may be present. Examples are given of the dehairing by enzymic means and subsequent enzymic bating of: (1) dry goatskins, (2) salted sheepskins, (3) salted calfskins.

Gelatin Product and Process of Manufacture. U. S. Pat. 2,851,364. David D. Peebles, Davis, Calif., assignor to Foremost Dairies, Inc., San Francisco, Calif., a corporation of New York. Appl. June 21, 1956.



1. In a process for the manufacture of a dry gelatin product, dry mixing powdered gelatin with powdered lactose, adding moisture to the particles of the mix to make them sticky causing the particles to contact and adhere together in the form of moist porous aggregates, and removing excess moisture from the aggregates.

Synthetic Tanning Agents. Brit. Pat. 796,905. Badische Anilin- & Soda-Fabrik Akt.-Ges. Appl. June 20, 1956.—Leather is tanned or after-treated by a condensation product of a polyfunctional urethane with formaldehyde formed by reacting a dihydroxy primary alcohol with urea to give a diurethane and then reacting the resultant melt with formaldehyde. Smaller amounts of dihydroxy secondary or polyhydroxy alcohols such as 1:3- or 2:3-butylene glycol, trimethylol-propane, butane-triol, hexane-triol, erythritol and glycerine may be built into the condensation product. Dihydroxy primary alcohols employed may be propane-diol-(1:3), butane-diol-(1:4), pentane-diol-(1:5), hexane-diol-(1:6), diethylene glycol, dihydroxydibutyl ether and dihydroxydiethyl sulphide. The resulting compound may be used as a monomolecular compound or as a low molecular weight condensation product. The condensation product may be used in acid, neutral or alkaline solution and urea may be added. In examples: (1) a condensation product of formaldehyde and alpha-delta-butane-diurethane (A) is used to treat calf-hide in a sodium carbonate solution; (2) calf-hide is treated with (A) in a solution of formic acid and sodium chloride (*p*H 2.3); (3) rabbit skin is treated with (A) in a solution of formic acid and sodium chloride or in sodium carbonate solution; (4) neat's leather is after-treated with (A) in a solution of formic acid and sodium chloride (*p*H 2.3).

Process of Tanning with Malonaldehyde or Succinaldehyde and Optionally Mineral Tanning Agent and Leather Produced Thereby. U. S. Pat. 2,851,329. Ludwig Seligsberger, Newton, Mass., assignor to the United States of America as represented by the Secretary of the Army. Appl. Nov. 18, 1955.—In the production of leather from hide, the process of tanning said hide with an aqueous solution of an aliphatic dialdehyde having at least three carbon atoms in the molecule, said dialdehyde being a member of the group consisting of malonaldehyde and succinaldehyde, said solution having a pH between about 2.5 and about 5, and a mineral tanning agent.

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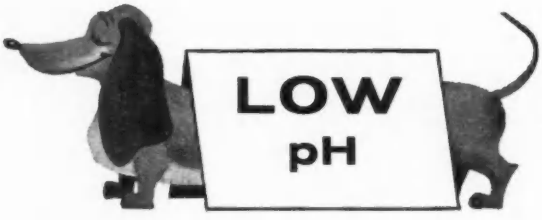

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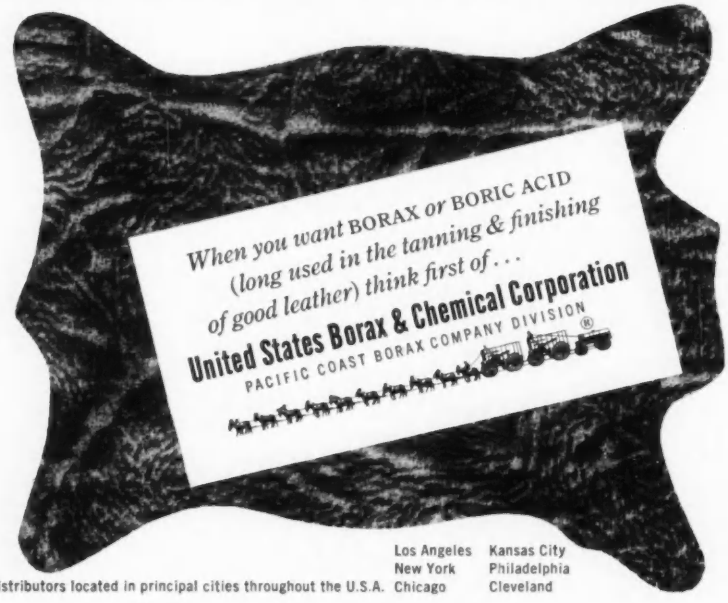
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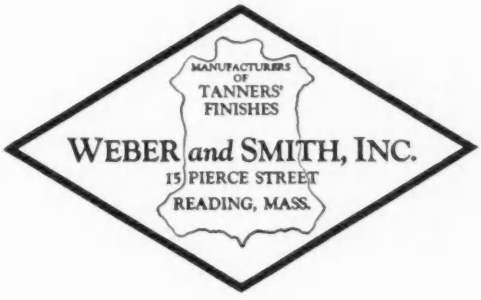

INDEX TO ADVERTISERS

ADOLF SCHUBERT XXXVIII
AMERICAN CYANAMID COMPANY, Dyestuff Department XVII
APEX CHEMICAL CO., INC. XXX
ARKANSAS COMPANY, INC. VI
ARTHUR C. TRASK CO. XV
ARTHUR THOMAS CO. XXII
ATLAS REFINERY XVI
AULSON TANNING MACHINERY CO., THE XXXVIII
A. W. HOPTON XXXVII
BARKEY IMPORTING CO., INC. XIV
BARIUM REDUCTION CORPORATION XI
BONA ALLEN, INC. XXXVIII
BUCKMAN LABORATORIES, INC. IV
BUFFALO EXTRACT & SUPPLY CO. XXXIX
CALGON COMPANY XXXVII
CHEMTAN COMPANY ..... Outside Back Cover
EASTERN INDUSTRIAL OIL PRODUCTS CO. XXXVI
E. F. DREW & CO., INC. XXX
EISENDRATH TANNING CO. XXIX
EUROPEAN MANUFACTURERS OF CHESTNUT EXTRACTS X
FIBER CHEMICAL CORPORATION XXXV
FRANK F. MARSHALL XXXIII
GARDEN STATE TANNING, INC. XXXIII
GEIGY COMPANY, INC. IX
GENERAL DYESTUFF COMPANY ..... XII – XIII
HOOKER CHEMICAL CORP. XIX
HOWES LEATHER CO., INC. XXXVIII
INTERNATIONAL SALT CO., INC. V
JOHNSON AND CARLSON XXXV
KEPEC CHEMICAL CORPORATION XXXIII
LEATHER AND SHOES XXVII
LEATHER MANUFACTURER, THE XXXI
L. H. LINCOLN & SON, INC. XX
LOWELL TECHNOLOGICAL INSTITUTE XXXIX
MARDEN WILD CORPORATION XXXII
NEWARK LEATHER FINISH CO. XXXIV
NOPCO CHEMICAL CO. XXIII
OHIO LEATHER CO., THE XXIX
OLSON IMPORTING COMPANY, INC., THE ..... Inside Front Cover
ORTHMANN LABORATORIES, INC., THE XXIX
PRESTO COLOR CO. XXVIII
PRIME LEATHER FINISHES CO. XXXIII
PROCTOR AND SCHWARTZ, INC. XXXVI
REILLY-WHITEMAN-WALTON CO. XXXI
ROBESON PROCESS CO. II
ROHM & HAAS VIII
SALEM OIL & GREASE CO. XXXII
SAXE CUTCH CORPORATION XXX
SEABOARD CHEMICALS, INC. ..... Inside Back Cover
SOCONY MOBIL OIL CO., INC. XXI
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL CORP. ..... XXV — XXVI
SUN OIL COMPANY XXIX
TANIMEX CORPORATION III
TANNADE COMPANY XXXV
TANNER'S COUNCIL RESEARCH LABORATORY ..... XXX — XXXIII — XXXVII
UNITED STATES BORAX & CHEMICAL CORP. XXVIII
UNITED STATES TESTING COMPANY XXXIV
WALLERSTEIN COMPANY, INC. XXIV
WARNER CO. XXXII
WEBER & SMITH, INC. XXXIX
WHITTEMORE-WRIGHT CO. XXVIII
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XVIII

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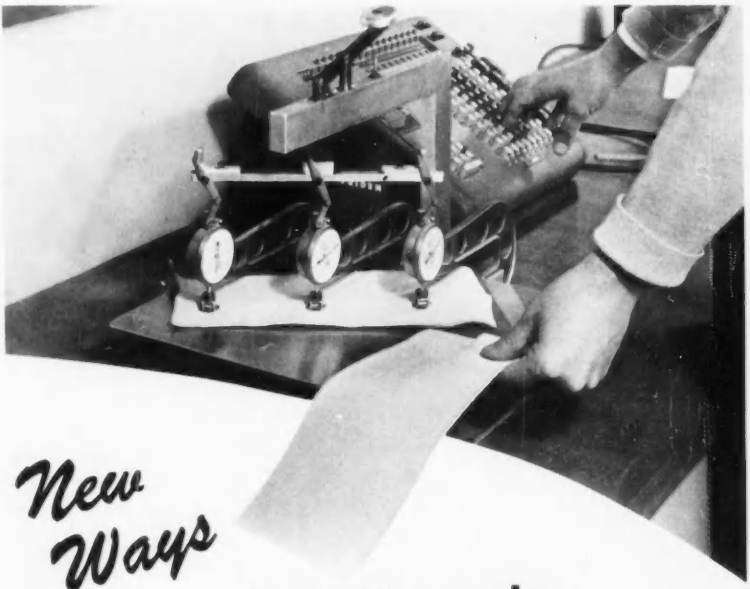

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All our facilities are devoted exclusively to the tanning industry